

HYDROGEN STORAGE IN METAL-DECORATED NANOSTRUCTURED MATERIALS

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Introduction

Hydrogen is regarded as one of the clean energy sources in the future. It is free of CO₂ and its energy efficiency is, if used together with the hydrogen fuel cell, highest among all known technologies so far. Currently, the storage of hydrogen is a bottleneck for the development of hydrogen fuel-cell powered vehicles and it is essential to design a safe and efficient hydrogen storage system operated under ambient conditions on-board vehicles. Solid-state storage is highly desirable for the purpose of safety and there are two different categories in the solid-state storage. One is the storage in metal or chemical hydrides in the form of dissociated (atomic) hydrogen and the other is the storage in nanostructured materials in the form of non-dissociated (molecular) hydrogen. Here, we concentrate on the molecular storage taking advantage of relatively weak interactions between molecular hydrogen and the host materials.

Results and Discussion

Through first-principles electronic structure calculations, we search for hydrogen storage media among carbon-based nanostructured materials decorated with extra metal atoms[1,2]. In the systems we study, metal atoms are bound to a porous backbone material and hydrogen molecules are stored by being attached to those metal atoms. We have reported some of these results in the literature[3,4] and recent conferences.

Transition metal atoms can bind hydrogen molecules through the simultaneous electron donation and back-donation which is called a "Kubas interaction". This interaction is extremely useful for the room-temperature hydrogen storage

applications and provides the optimal H₂ binding energy of 0.3eV including the zero-point energy correction. Figure 1 shows a schematic example of such an interaction in the case of Ti-decorated propane 1,3-diol with 4H₂ molecules adsorbed on it. We show that there exists competition between the exchange field and the ligand(crystal) field splitting, and the high storage capacity is achievable when the ligand field dominates. We note that the transition metal atom, which was originally in a high-spin state, now shifts to a low-spin state with surrounding hydrogen molecules producing the ligand field. Such a spin-flip turns out to contribute to the binding energy of H₂ significantly. Figure 1 demonstrates an unusual feature in the hybridization between the Ti d and H₂ s orbitals. Attachment of 4H₂ molecules on a Ti atom at the center is shown in Fig. 1(a) as an example.

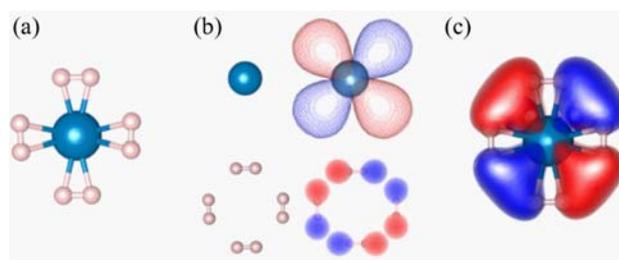


Figure 1. Ti-4H₂ system. (a) 4H₂ molecules(smaller balls) attached on a Ti atom(larger blue ball). (b) Ti d_{xy} orbital and H₂ sigma antibonding orbitals. (c) hybridization of the orbitals in (b).

It is common that the occupied H₂ sigma bonding orbital hybridizes with unoccupied Ti d orbitals. This is called an electron donation channel. What is unusual here is that the unoccupied H₂ sigma antibonding orbital(the bottom figure of Fig. 1(b)) matches with an occupied Ti d orbital(d_{xy})(the top figure of Fig. 1(b)) in phase. Two overlapping orbitals hybridize well as shown in Fig. 1(c). Now

the charge transfer is opposite (from Ti d to H₂ sigma antibonding) and this is called a back-donation channel. Other metal atoms such as calcium may bind hydrogen molecules through the dipole interaction as well which is induced by the ionization of the metal atoms. In particular, if two carbon atoms in the hexagonal ring of the backbone structure are replaced by Boron atoms, the binding energy may be increased significantly (both Ca-backbone and the H₂-Ca binding).

Metal clustering and oxidation are found to be serious problems in synthesizing ideal storage materials. New decorating methods such as functionalization of the backbone materials (with OH, for instance) and new decorating metals such as Ca and Fe are proposed to overcome these problems. In Fig. 2, as a simple model system, a propane molecule is functionalized with the hydroxyl group (OH), and an iron (Fe) atom is inserted between OH. Then up to 4H₂ molecules may be bound via the Kubas interaction. Such an idea is further developed to design a Fe-decorated OH-functionalized metal-organic framework (MOF).

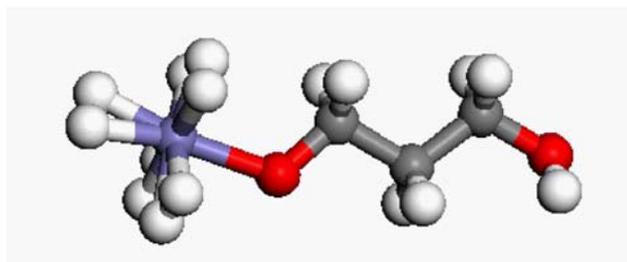


Figure 2. H₂ adsorption on the Fe-decorated molecule. The blue, red, grey, and white balls represent Fe, O, C, and H atoms, respectively.

We propose to use IRMOF 16 for that purpose [4] and its structures before and after H₂ storage are shown in Fig. 3(a) and (b). The H₂ molecules stored in the void volume at the center are not shown for visual clarity. Our grand canonical Monte Carlo simulation indicates that such a system stores 6 wt% hydrogen in total (including the storage in the void volume) under ambient conditions. Such a large storage capacity at room temperature is possible because the H₂ binding energy to the Fe-decorated MOF is close to the optimal value (~0.3 eV/H₂). It remains to be an experimental challenge how to synthesize a stable Fe-decorated system.

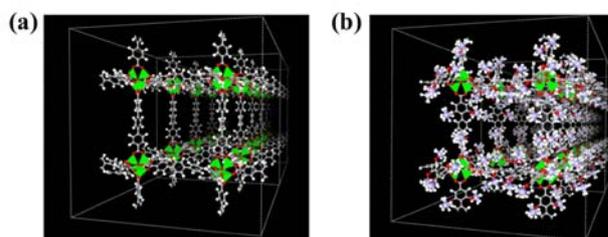


Figure 3. H₂ adsorption on Fe-decorated MOF. (a) IRMOF 16 before H₂ adsorption. (b) Fe-decorated, OH-functionalized IRMOF after H₂ adsorption according to grand canonical Monte Carlo simulations.

References

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